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VISCOELASTICITY RESEARCH GROUP

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**THERMODYNAMIC THEORY OF
ELASTIC RELAXATION**

by

Josef Meixner

Translated by Mrs. Jane A. C. Burlak

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NORTH CAROLINA STATE COLLEGE
SCHOOL OF PHYSICAL SCIENCES AND APPLIED MATHEMATICS
SCHOOL OF ENGINEERING
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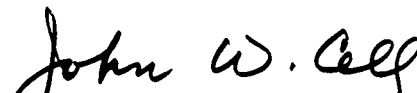
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THERMODYNAMIC THEORY OF ELASTIC RELAXATION

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(Z. Naturforschg. 9a, 654-663 [1954]; received on May 11th, 1954).

Assuming that the relaxation phenomena of a system may be described by the introduction of internal variables and the application of the thermodynamics of irreversible processes, general properties of relaxing systems with arbitrarily many external variables are examined. In particular, the transition to the after-effect theory of relaxation phenomena is carried out, several properties of the after-effect matrix and its Laplace transforms are stated and proved, the thermodynamic potentials are expressed in terms of the after-effect functions and two general theorems on relaxation spectra are proved. The discussion is carried through for the case of elastic relaxation taking into account the most general properties of viscoelastic bodies; the discussion can immediately be extended to dielectric relaxation.

1. General Remarks on After-effect Theory.

The after-effect theory of relaxation phenomena reached a certain stage in the works of Gross¹ and Hiedemann and Spence² (in ¹ and ² the earlier literature on this problem is surveyed) for the most important case, namely that of the isothermal or adiabatic after-effect between two conjugate thermodynamic variables. As for the mechanisms of the molecular phenomena at the root of the after-effect, there are few quantitative results even in cases where the mechanisms have been clarified to some extent. However, even if one neglects the nature of the mechanisms and examines the after-effect theory only in its phenomenological form, there are still many open questions. Some more recent work does deal with the tensorial formulation

1 B. Gross, Mathematical Structure of the Theories of Viscoelasticity, Paris, 1953.

2 E. Hiedemann and R. D. Spence, Z. Physik 133, 109[1952].

of the after-effect theory, for example Sips³ and, in particular, Takizawa⁴ in connection with the research of Frenkel and Obrastzov⁵ and of Oshida⁶; however, they restrict themselves to isotropic bodies and only Takizawa drops the adiabatic condition or the isothermal condition; he also includes in his consideration the temperature after-effect, thereby taking a first step in the direction of a thermodynamical after-effect theory. However, what is still missing is, 1) the formulation of a thermodynamical theory which, in addition to the after-effect of the temperature or entropy, includes the after-effect of stress and strain; 2) the investigation of the properties of the after-effect matrix, which here replaces a single after-effect function; 3) the characterization of the energy conditions within the framework of the after-effect theory (a first step in this direction has been taken by Stavermann and Schwarzl⁷); 4) the replacement of the after-effect standpoint by the introduction of suitable internal variables and the interpretation of the after-effect as the result of taking limits with the internal variables tending to their equilibrium values; and finally 5) the investigation of the tensorial properties of these internal variables, in particular in anisotropic crystals. Finkelstejn and Fastov⁸ have made an important contribution to the last problem for isotropic bodies by the introduction of the relaxation tensor.

A series of these problems is dealt with in this paper for a special case of the general after-effect theory, namely for the case which is concerned with the thermodynamics of irreversible processes. The theory corresponding to this is the so-called thermodynamic theory of relaxation

3 R. Sips, J. Polymer Sci. 7, 191[1951].

4 E. I. Takizawa, Mem. Fac. Engng., Nagoya Univ. 5, 1[1953].

5 I. Frenkel and J. Obrastzov, J. Phys. Chem. USSR 2, 131[1940].

6 I. Oshida, Mem. Fac. Engng., Nagoya Univ. 2, 29[1950].

7 A. J. Stavermann and F. Schwarzl, Proc. Roy. Soc., Amsterdam B55, 474, 486[1952].

8 B. N. Finkelstejn and N. S. Fastov, Dokl. Akad. Nauk. SSSR, n.S. 71, 875[1950].

phenomena^{9,10}. It starts from the assumptions 1) that the thermodynamic state of the material concerned may be represented approximately by the internal energy as a function of the entropy, of the strain components and of certain internal variables which describe the possible internal changes (chemical reactions in the most general sense); 2) that the usual thermodynamic formalism yields conjugate variables, specifically the temperature, the stress components and the fluxes corresponding to the internal variables and finally 3) that the variation of the internal variables with respect to time are linear homogeneous functions of the fluxes.

All the considerations can be carried over without difficulty to the electrical after-effect; to do this it is only necessary to re-interpret the symbols and formulae.

2. Thermodynamics of the Anisotropic Elastic Body.

We consider next an anisotropic body in thermodynamical equilibrium; this can be unconstrained or constrained or also in the sense of Schottky¹¹ imaginarily constrained. We denote the components of the stress tensor $\sigma_{xx}, \sigma_{yy}, \sigma_{zz}, \sigma_{yz}, \sigma_{zx}, \sigma_{xy}$, by the series $\sigma_1, \sigma_2, \sigma_3, \sigma_4/\sqrt{2}, \sigma_5/\sqrt{2}, \sigma_6/\sqrt{2}$, and the components of the corresponding strain tensor $\epsilon^1, \epsilon^2, \epsilon^3, \epsilon^4/\sqrt{2}, \epsilon^5/\sqrt{2}, \epsilon^6/\sqrt{2}$. Hence we have approximately $\epsilon^4/\sqrt{2} = \epsilon_{yz} = 1/2(\partial v/\partial z + \partial w/\partial y)$, if v, w are the y - and z -components of the displacement. With this notation the quantities

$$\sum_{i=1}^6 \sigma_i \sigma_i, \quad \sum_{i=1}^6 \epsilon^i \sigma_i, \quad \sum_{i=1}^6 \epsilon^i \epsilon^i \quad (1)$$

are invariant under every rotation of the x, y, z coordinate system.

The state of the body is determined if we are given 1) the σ_i and the temperature T , or 2) the ϵ^i and the entropy s per unit volume, or

9 J. Meixner, Z. Naturforschg. 4a, 594[1949].

10 J. Meixner, Kolloid-Z 134, 3[1953].

11 W. Schottky, Thermodynamik, Berlin 1929, p. 65.

3) the ε^i and T or 4) the σ_i and s . As reference state, we denote the stress- and strain-free state by the temperature T^+ ; it can also be characterized by the corresponding entropy s^+ per unit volume. We always assume that all the variations from the reference state i.e. all ε^i , σ_i , $s - s^+$, $T - T^+$ are so small that linear relations exist between these quantities. We get a compact notation if we denote $s - s^+$ by ε^0 and $T - T^+$ by σ_0 . Then all the σ_i ($i = 0, 1, \dots, 6$) are intensive variables and all the ε^i ($i = 0, 1, \dots, 6$) are specific (i.e. referred here to the unit volume) values of extensive variables.

For the internal energy u , the free energy f and the free enthalpy g , at any given time referred to the unit volume, the following differential relations are valid

$$du = Tds + \sum_{i=1}^6 \sigma_i d\varepsilon^i = T^+ d\varepsilon^0 + \sum_{i=1}^6 \sigma_i d\varepsilon^i, \quad (2)$$

$$df = -sdT + \sum_{i=1}^6 \sigma_i d\varepsilon^i = -s^+ d\sigma_0 + \sum_{i=1}^6 \sigma_i d\varepsilon^i - \varepsilon^0 d\sigma_0, \quad (3)$$

$$dg = -sdT - \sum_{i=1}^6 \varepsilon^i d\sigma_i = -s^+ d\sigma_0 - \sum_{i=1}^6 \varepsilon^i d\sigma_i. \quad (4)$$

In what follows, unless otherwise indicated, the following summation convention is now observed: - any latin index occurring twice in a product is to be summed from 1 to 6 or from 0 to 6 respectively according as to whether it has the upper index ' or not; for the Greek indices which arise later, summation is similarly over all internal changes.

In the domain of validity of Hooke's law extended to anisotropic bodies and with, moreover, small variations from the reference state, the internal energy can be expanded to a first approximation as

$$u - u^+ = T^+ \varepsilon^0 + 1/2 c_{ik} \varepsilon^i \varepsilon^k \quad (5)$$

$$\text{where} \quad c_{ik} = c_{ki} \quad (i, k = 0, 1, \dots, 6) \quad (6)$$

Hence we have, from (2), the linear relations

$$\sigma_i = c_{ik} \varepsilon^k \quad (i = 0, 1, \dots, 6) \quad (7)$$

with their converse ($c^{ik} = c^{ki}$ is the inverse matrix of c_{ik})

$$\varepsilon^i = c^{ik} \sigma_k \quad (i = 0, 1, \dots, 6). \quad (8)$$

For brevity, we call c_{ik} the thermoelastic matrix.

There then results for the free energy and the free enthalpy

$$f - f^+ = -s^+ \sigma_0 + \frac{1}{2} (c_{i'k'} - \frac{c_{oi'} c_{ok'}}{c_{oo}}) \varepsilon^{i'} \varepsilon^{k'} + \frac{c_{i'o}}{c_{oo}} \varepsilon^{i'} \sigma_0 - \frac{1}{2c_{oo}} \sigma_0 \sigma_0, \quad (9)$$

$$g - g^+ = -s^+ \sigma_0 - \frac{1}{2} c^{ik} \sigma_i \sigma_k. \quad (10)$$

The quantities u^+ , f^+ , g^+ are here the internal energy, free energy and free enthalpy of the reference state.

In (8) we have assumed that the ε^i are uniquely determined from the σ_i and conversely (i.e. that the determinants of the matrices c_{ik} and c^{ik} are different from zero). Then it follows, in addition, that the quadratic forms

$$c_{ik} x_i x_k \quad \text{and} \quad c^{ik} x_i x_k$$

in the real variables x_i are positive definite. To prove this, we start from the fact that the internal energy of the adiabatically strained body with $\varepsilon^0 = 0$ and the free energy of the isothermally strained body with $\sigma_0 = 0$ are greater than the internal energy and the free energy respectively of the reference state. Hence the quadratic forms

$$c_{i'k'} x_{i'} x_{k'} \quad \text{and} \quad (c_{i'k'} - \frac{c_{oi'} c_{ok'}}{c_{oo}}) x_{i'} x_{k'}$$

in six variables are positive definite and it follows that

$$c_{ik} x_i x_k = (c_{i'k'} - \frac{c_{oi'} c_{ok'}}{c_{oo}}) x_{i'} x_{k'} + \frac{1}{c_{oo}} (c_{ok} x_k)^2 > 0,$$

if the x_i are real and not all equal to zero; for c_{oo} is the inverse thermal capacity per unit volume under constant strain and this is positive because of the internal thermodynamical stability. A further statement of the internal thermodynamical stability conditions, which imply $c_{ik} x_i x_k > 0$ for

$$x_1 = x_2 = x_3, x_4 = x_5 = x_6 = 0,$$

$$x_0, x_1 = \text{real}, \quad |x_0| + |x_1| \neq 0,$$

does not require to be taken into consideration separately, since it only describes a special case of the positive definite character of the quadratic form $c_{ik}x_i x_k$ which has already been proved. In the same way as c_{ik} belongs to a positive definite quadratic form so also does c^{ik} by known theorems.

3. Consideration of Internal Changes.

We now extend our investigations to an elastic body, in which internal changes are possible and whose state is therefore not only described by the ε^i or by the σ_i or a certain choice of seven of the quantities ε^i , σ_i with different indices, but whose internal state we have still to characterize by so-called internal variables. These can be the fluxes of the internal changes or concentrations of independent components or any linearly independent combinations of these quantities. It simplifies the notation if we assume the reference state, now also to be characterized with respect to the internal variables, to be stress- and strain-free and in perfect thermodynamic equilibrium with respect to the internal changes; of course, this requires it to be perfect only with respect to changes which can take place inside the period of observation; other changes can be regarded as not permissible, their fluxes are taken into the thermodynamic potentials and relations as constant with respect to time. In considering the internal variables we shall also limit ourselves to the neighbourhood of equilibrium and we denote by ξ^a the deviations of the internal variables from the equilibrium values corresponding to the reference temperature T^+ ; from now on we call these differences ξ^a the internal variables. If the number of internal changes is n , the index a then runs from 1 to n . The case $n = \infty$ is not excluded; it is then assumed that the infinite series which occurs is convergent.

Then for the internal energy it follows, generalizing (5) and restricting terms to those which are at most of second order of smallness, with $c_{ik} = c_{ki}$ and $r_{a\beta} = r_{\beta a}$,

$$u - u^+ = T^+ \varepsilon^0 + \frac{1}{2} c_{ik} \varepsilon^i \varepsilon^k + q_{ia} \varepsilon^i \xi^a + \frac{1}{2} r_{a\beta} \xi^a \xi^\beta. \quad (11)$$

The coefficients c_{ik} , q_{ia} , $r_{a\beta}$ depend only on the reference state, i.e. on T^+ or s^+ respectively. In place of the differential relation (2) there now holds more generally

$$du = T^+ d\varepsilon^0 + \sigma_i d\varepsilon^i - A_a d\xi^a \quad (12)$$

where the coefficients A_α are called fluxes. Then from (11) and (12) follow the linear relations

$$\begin{aligned}\sigma_i &= c_{ik} \varepsilon^k + q_{ia} \xi^a \quad (i = 0, 1, \dots, 6), \\ A_\alpha &= -q_{k\alpha} \varepsilon^k - r_{\alpha\beta} \xi^\beta \quad (\alpha = 1, 2, \dots, n).\end{aligned}\tag{13}$$

For given values ε^k , one finds the equilibrium values of the ξ^a by minimizing the internal energy or equivalently by taking the fluxes A_α to be zero. Since the equilibrium value of the internal energy (i.e. its minimum for variation of the ξ^a from the result of the last section for $\varepsilon^0 = 0$) is greater than u^+ , except if all ε^i vanish, then the quadratic form in the $7 + n$ variables ε^i, ξ^a

$$\frac{1}{2} c_{ik} \varepsilon^i \varepsilon^k + q_{ia} \varepsilon^i \xi^a + \frac{1}{2} r_{\alpha\beta} \xi^a \xi^\beta\tag{14}$$

is first of all for $\varepsilon^0 = 0$ positive definite; from analogous properties of the free energy one then concludes, as in the preceding section, that the quadratic form (14) in all the variables ε^i and ξ^a is positive definite.

c_{ik} now denotes the thermoelastic matrix with 49 components for hidden coordinates, i.e. for ξ^a held constant. In the thermodynamic equilibrium with $A_\alpha = 0$, it follows from (11) by elimination of the ξ^a using (13) that

$$u - u^+ = T^+ \varepsilon^0 + \frac{1}{2} (c_{ik} - q_{ia} r^{\alpha\beta} q_{k\beta}) \varepsilon^i \varepsilon^k,\tag{15}$$

if $r^{\alpha\beta}$ is the reciprocal matrix of $r_{\alpha\beta}$. The thermoelastic matrix for unconstrained equilibrium therefore reads $c_{ik} - q_{ia} r^{\alpha\beta} q_{k\beta}$; also it belongs to a positive definite quadratic form, and for viscoelastic bodies (see below) to a positive semi-definite quadratic form.

Now there are some particular cases still to be investigated. If $\det |r_{\alpha\beta}| = 0$, then one can introduce as new internal variables homogeneous linear functions of the original variables ξ^a , in such a way that $r_{\alpha\beta} \xi^a \xi^\beta$ transforms into a quadratic form with fewer than n variables; also $q_{ia} \varepsilon^i \xi^a$ then contains no more of the same new internal variables than $r_{\alpha\beta} \xi^a \xi^\beta$. The quadratic form (14) is then only semi-definite, but after re-arranging to the reduced number of new internal variables is again positive definite. We therefore do not restrict the generality if we assume (14) positive definite. This means that the internal variables may always

be decomposed by a suitable choice into some which go into a positive definite quadratic form $\frac{1}{2} r_{\alpha\beta} \xi^{\alpha} \xi^{\beta}$ in $u - u^{+}$ and others which generally do not appear in $u - u^{+}$.

We get a borderline case if we allow the body being considered to exhibit the property of viscoelasticity. Then the internal energy in the unconstrained thermodynamic equilibrium can be the same for different deformations; thus the internal energy of the isotropic, viscoelastic body in equilibrium does not depend on the shear deformation, but only on the volume, i.e. on $\varepsilon^1 + \varepsilon^2 + \varepsilon^3$. The quadratic form of the matrix $c_{ik} - q_{ia} r^{\alpha\beta} q_{k\beta}$ is then semi-definite and its determinant is equal to zero; thus this case can exist even for the matrix c_{ik} . However, in the following, we want to consider exclusively those bodies which in constrained equilibrium (i.e. for constant ξ^{α} or, expressed in another way, for fast stresses, possess no viscous behavior, but have purely elastic properties. Then we can always assume $\det |c_{ik}| \neq 0$ and the existence of the matrix c^{ik} , the reciprocal of c_{ik} , with $\det |c^{ik}| \neq 0$.

Besides the internal energy (11) we still estimate the free energy and the free enthalpy, as they can be calculated from their definitions using (13). These are, in suitable variables,

$$f - f^{+} = -s^{+} \sigma_0 - \frac{1}{2c_{00}} \sigma_0 \sigma_0 + \frac{c_{i'0}}{c_{00}} \sigma_0 \varepsilon^{i'} + \frac{1}{2} (c_{i'k'} - \frac{c_{oi'} c_{ok'}}{c_{00}}) \varepsilon^{i'} \varepsilon^{k'} + \frac{q_{0\alpha}}{c_{00}} \sigma_0 \xi^{\alpha} + (q_{i\alpha} - \frac{c_{oi'}}{c_{00}} q_{0\alpha}) \varepsilon^{i'} \xi^{\alpha} + \frac{1}{2} (r_{\alpha\beta} - \frac{q_{0\alpha} q_{0\beta}}{c_{00}}) \xi^{\alpha} \xi^{\beta} \quad (16)$$

$$g - g^{+} = -s^{+} \sigma_0 - \frac{1}{2} c^{ik} \sigma_i \sigma_k + q_a^i \sigma_i \xi^a + \frac{1}{2} \bar{r}_{\alpha\beta} \xi^{\alpha} \xi^{\beta} \quad (17)$$

$$\text{with } q_a^i = c^{ik} q_{ka}, \bar{r}_{\alpha\beta} = r_{\alpha\beta} - q_{ia} c^{ik} q_{ka} \quad (18)$$

Finally, ε^0 can be calculated from (11) as a function of $u - u^{+}$, $\varepsilon^{k'}$, ξ^{α} to an equivalent approximation, i.e. including the quadratic terms

$$\varepsilon^0 = \frac{1}{T^{+}} (u - u^{+}) - \frac{c_{00}}{2T^{+3}} (u - u^{+})^2 - \frac{c_{ok'}}{T^{+2}} (u - u^{+}) \varepsilon^{k'} - \frac{c_{i'k'}}{T^{+}} \varepsilon^{i'} \varepsilon^{k'} - \frac{q_{0\alpha}}{T^{+2}} (u - u^{+}) \xi^{\alpha} - \frac{q_{i'a}}{T^{+}} \varepsilon^{i'} \xi^{\alpha} - \frac{r_{\alpha\beta}}{2T^{+}} \xi^{\alpha} \xi^{\beta}. \quad (19)$$

Using the differential relations (2), (3) and (4), one again obtains the linear relations (13) between both sets of conjugate variables in a different form. Then it follows from (17) that

$$\begin{aligned}\mathcal{E}^i &= c^{ik} \sigma_k - q_a^i \xi^a (i = 0, 1, \dots, 6), \\ A_a &= q_a^k \sigma_k - \bar{r}_{a\beta} \xi^\beta (a = 1, 2, \dots, n),\end{aligned}\tag{20}$$

while (19) leads exactly to the equations with $\frac{u - u^+}{T^+}$ in place of \mathcal{E}^0 .

Now the thermodynamic relations can be completed using the relations which describe the change with respect to time of the internal variables ξ^a . Since the $d\xi^a/dt$ vanish for $A_a = 0$, i.e., for thermodynamic equilibrium, then we can obviously express the $d\xi^a/dt$, at least in the neighbourhood of equilibrium (which is always assumed here), as linear functions of the A_a

$$\frac{d\xi^a}{dt} = E^{a\beta} A_\beta \quad (a = 1, 2, \dots, n).\tag{21}$$

This substitution gives exactly the thermodynamics of irreversible processes^{9,12} and it says moreover that the Onsager's reciprocity relations

$$E^{a\beta} = E^{\beta a}\tag{22}$$

are valid.

Also the matrix $E^{a\beta}$ belongs to a positive definite quadratic form, if generally we have thermodynamic equilibrium for fixed \mathcal{E}^i or σ_i . The quadratic form $A_a d\xi^a/dt = E^{a\beta} A_a A_\beta$ cannot assume negative values, for it denotes the local entropy generation; however, if it were semi-definite, then its determinant would vanish and it would give a linear combination of the ξ^a , which remains constant with respect to time and can be different from zero. Hence we can also write (21), by introducing the matrix $E_{a\beta}$ which is the reciprocal of $E^{a\beta}$ and with $E_{a\beta} = E_{\beta a}$, as follows

$$E_{a\beta} \frac{d\xi^\beta}{dt} = A_a \quad (a = 1, 2, \dots, n).\tag{23}$$

¹² J. Meixner, Z. phys. Chemie B 53, 253[1943]; Ann Phys. (5) 43, 244[1943].

4. Transition to the After-effect Interpretation.

The change with respect to time of the state of the material considered depends in the thermodynamic theory of relaxation phenomena, which has just been discussed, only on the instantaneous state, i.e. on the totality of independent variables describing the state. Therefore these are here perhaps the ε^i and the ξ^a . The change with respect to time of the conjugate quantities σ_i is certainly no longer determined if one does not know the ξ^a , unless one knows other measures of the system besides the ε^i at the instant concerned; the ε^i at earlier instants would be suitable. We get just such a representation of the σ_i if we eliminate the ξ^a in the relations of the last section. For this purpose we start from the 2nd equation in (13) and eliminate now the A_a using (23). We obtain, with the notation $d/dt = D$,

$$(r_{a\beta} + E_{a\beta}D) \xi^\beta = -q_{ka} \varepsilon^k. \quad (24)$$

We denote by $\Phi^{a\beta}(D)$ the operator matrix which is the reciprocal of $r_{a\beta} + E_{a\beta}D$; by substituting for ξ^β from (24) in the first equation (13), there results

$$\sigma_i = [c_{ik} - q_{ia} \Phi^{a\beta}(D) q_{k\beta}] \varepsilon^k. \quad (25)$$

The structure of this equation becomes considerably clearer if we make use of the fact that both the symmetric matrices $r_{a\beta}$ and $E_{a\beta}$ with positive definite quadratic form can be transformed by a real matrix $T_{a\cdot}^{\cdot\beta}$ into diagonal form. Therefore let

$$\begin{aligned} T_{a\cdot}^{\cdot\beta} (r_{\beta\gamma} + E_{\beta\gamma}D) T_{\varepsilon\cdot}^{\cdot\gamma} &= (1 + \tau_a D) \delta_{a\varepsilon} \\ &= \begin{cases} 1 + \tau_a D & \text{for } a = \varepsilon \\ 0 & \text{for } a \neq \varepsilon \end{cases} \end{aligned} \quad (26)$$

be universally valid in D with positive τ_a , the so-called relaxation times for constant ε_i . Then it follows that

$$\Phi^{a\beta}(D) = \frac{T_{\gamma\cdot}^{\cdot a} T_{\gamma\cdot}^{\cdot \beta}}{1 + \tau_\gamma D} \quad (27)$$

and with the abbreviation

$$q_{ia} T_{\gamma}^{\alpha} = Q_{i\gamma} \quad (28)$$

from (25)

$$\sigma_i = \left[c_{ik} - \frac{Q_{i\gamma} Q_{k\gamma}}{1 + \tau_{\gamma} D} \right] \varepsilon^k \quad (29)$$

This transformation to principal axes therefore effects the partial fraction decomposition of the operator $\Phi^{\alpha\beta}(D)$. The relation (29) becomes, after multiplication by the denominators $1 + \tau_{\gamma} D$, a dynamic thermoelastic relation between the σ_i and the ε^i together with their derivatives up to n th order. It is an extension of the well-known dynamical equation of state of acoustics¹³.

From (29) we now come immediately to the relationship between the σ_i and the ε^i in the sense of the after-effect theory. For any function $x(t)$, it is true that

$$x(t) = (1 + \tau D) \int_0^{\infty} \frac{e^{-v/\tau}}{\tau} x(t - v) dv \quad (30)$$

and hence we can transform (29) to

$$\sigma_i(t) = c_{ik} \varepsilon^k(t) - \int_0^{\infty} c_{ik}(v) \varepsilon^k(t - v) dv, \quad (31)$$

with

$$c_{ik}(v) = \sum_{\gamma} Q_{i\gamma} Q_{k\gamma} \cdot \frac{e^{-v/\tau_{\gamma}}}{\tau_{\gamma}} \quad (32)$$

First of all note that (29) is a system of inhomogeneous differential equations for the $\sigma_i(t)$, as one recognizes by multiplying out the denominators $1 + \tau_{\gamma} D$. (31) is only a particular integral of this inhomogeneous system of equations; however, it describes the behavior of the system of interest to us, because one may always regard the solutions which are decreasing exponentials with respect to time as having died out, if one has left the system to itself for long enough before the start of an experiment.

13 L. I. Mandelstam and M. A. Leontovitsch, J. Exp. Theor. Phys. U.S.S.R. 7, 438[1937].

Meantime we start from equation (20) instead of from equation (13) and again eliminate the ξ^a , and obtain analogously

$$\varepsilon^i(t) = c^{ik} \sigma_k(t) + \int_0^\infty c^{ik}(v) \sigma_k(t-v) dv, \quad (33)$$

where

$$c^{ik}(v) = \sum_{\gamma} Q^{i\gamma} Q^{k\gamma} \frac{e^{-v/\tau^\gamma}}{\tau^\gamma} \quad (34)$$

with real quantities $Q^{i\gamma}$ and positive relaxation times τ^γ for σ_i constant. Therefore we have here as the antithesis of the stress relaxation for constant strain [expressed by the minus sign in (32)] a retarded strain for constant stress. For this reason one frequently calls the τ^γ retardation times.

5. The Properties of the After-effect Matrix.

We consider in addition to the after-effect matrices $C_{ik}(v)$ and $C^{ik}(v)$, their Laplace transforms

$$\Gamma_{ik}(p) = \Gamma_{ki}(p) = \int_0^\infty e^{-pv} C_{ik}(v) dv = \frac{Q_{i\gamma} Q_{k\gamma}}{1 + \tau_\gamma p}, \quad (35)$$

$$\Gamma^{ik}(p) = \Gamma^{ki}(p) = \int_0^\infty e^{-pv} C^{ik}(v) dv = \frac{Q^{i\gamma} Q^{k\gamma}}{1 + \tau^\gamma p}. \quad (36)$$

If one starts with $\sigma_i = 0$, $\varepsilon^i = 0$ for $t < 0$ and constructs the Laplace transforms of equations (31) and (33), one recognizes that both the matrices $c_{ik} - \Gamma_{ik}(p)$ and $c^{ik} + \Gamma^{ik}(p)$ are reciprocals of one another. Hence we have

$$[c_{ik} - \Gamma_{ik}(p)][c^{kl} + \Gamma^{kl}(p)] = \delta_{il}. \quad (37)$$

The parametric value $p = 0$ corresponds to thermodynamic equilibrium, and the parametric value $p = \infty$ to the constrained equilibrium - realized during very fast changes of the ε^i (or of the σ_i respectively), in particular for periodic stress of very high frequency. The thermoelastic matrix for thermodynamic equilibrium is therefore $c_{ik} - \Gamma_{ik}(0)$; it has a non-negative quadratic form. In particular, it is positive definite if in the equilibrium not only the σ_i are uniquely determined by the ε^i , but also the inverse is

true. It is, however, positive semi-definite if the ε^i are no longer uniquely given by the σ_i ; then $\det |c_{ik} - \Gamma_{ik}(0)| = 0$. Thus this relation characterizes in general the viscoelastic behavior and indeed does so not only for isotropic materials, but also for single crystals. For isotropic materials, however, it follows in particular from the vanishing of this determinant that all third order minors also vanish and hence, that an isotropic material with this property for any shear deformation is viscoelastic.

The functions $\Gamma_{ik}(p)$ and $\Gamma^{ik}(p)$ are regular analytic functions except at $p = -1/\tau_Y$ and $p = -1/\tau^Y$ respectively. For the matrices $\Gamma_{ik}(p)$ and $\Gamma^{ik}(p)$ one easily obtains from (35) and (36) the following statements:

For real x_i and $\Re p \geq 0$ the quadratic forms $\Re \Gamma_{ik}(p) x_i x_k$ and $\Re \Gamma^{ik}(p) x_i x_k$ are non-negative definite. Under the same conditions the quadratic forms $\Re [c^{ik} + \Gamma^{ik}(p)] x_i x_k$, $\Re [c_{ik} - \Gamma_{ik}(p)] x_i x_k$ are positive definite, however for the last form with the restriction $p \neq 0$, if the body is viscoelastic. Finally, it is true for real x_i , which are not all zero and $\Re p > 0$ that

$$\Re \frac{1}{p} [c_{ik} - \Gamma_{ik}(p)] x_i x_k > \Re \frac{1}{p} [c_{ik} - \Gamma_{ik}(0)] > 0; \Re p [c^{ik} + \Gamma^{ik}(p)] > 0. \quad (38)$$

We shall return to the meaning of the last two statements, which are also true for materials whose after-effect properties no longer come under the thermodynamic theory of relaxation, in another connection.

The relationship between the ε^i and the σ_i is closely analogous to the relationship between the in-flowing currents in an electric 2m-pole ($m = 7$) and the applied voltages. If we associate the σ_i with the voltages and the $d\varepsilon^i/dt$ with the intensities of the currents of the 2m-pole then the impedance matrix of the electrical network corresponds exactly to the matrix $Z_{ik}(p) = \frac{1}{p} [c_{ik} - \Gamma_{ik}(p)]$. Therefore, if it is possible to realize the matrix $Z_{ik}(p)$ by a suitable network, we obtain an electrical model for the whole elastic and thermal behavior of our body. For the case $m = 1$ (with two conjugate variables) electrical models with 2-poles, in particular, RC-models with resistances and capacitances, have long been used as a means of visualizing relaxation phenomena.

We observe further that the after-effect functions $C_{ik}(v)$ and $C^{ik}(v)$ for real $v \geq 0$ belong to non-negative definite quadratic forms; this follows immediately from (32) and (34). Even more strictly, it is true that these quadratic forms

$$C_{ik}(v)x_i x_k \text{ and } C^{ik}(v)x_i x_k, \quad (39)$$

for those real x_i for which they are not identically zero in v , are strictly monotonically decreasing for $0 < v < \infty$; i.e. their n th differential coefficient is different from zero and has algebraic sign $(-1)^n$. This property is characteristic of the structure of the after-effect functions. From it, by a theorem on strictly monotonic functions, it follows that the quadratic form $C_{ik}(v)x_i x_k$ may be described as a Stieltjes integral

$$C_{ik}(v)x_i x_k = \int_0^\infty e^{-\lambda v} d[\phi_{ik}(\lambda)x_i x_k], \quad (40)$$

with the function $\phi_{ik}(\lambda)x_i x_k$ not monotonically decreasing in λ . A similar result is true for $C^{ik}(v)$. Let us restrict ourselves - something that is not too serious and corresponds to the case of discrete relaxation spectrum - to functions $\phi_{ik}(\lambda)$, which apart from jump discontinuities $\lambda_\gamma = 1/\tau_\gamma > 0$ are constant, then, at each jump discontinuity,

$$[\phi_{ik}(\lambda_\gamma + 0) - \phi_{ik}(\lambda_\gamma - 0)]x_i x_k$$

is non-negative definite, therefore

$$C_{ik}(v) = \sum_\gamma e^{-v/\tau_\gamma} R_{ik,\gamma} \quad (41)$$

where $R_{ik,\gamma}x_i x_k$ is a non-negative definite quadratic form for every γ . Then, however, $R_{ik,\gamma}$ may be represented as a sum of at most $s + 1$ (≤ 7) products

$$R_{ik,\gamma} = R_{i\gamma}^0 R_{k\gamma}^0 + R_{i\gamma}^1 R_{k\gamma}^1 + \dots + R_{i\gamma}^s R_{k\gamma}^s \quad (i, k = 0, 1, \dots, 6) \quad (42)$$

with real factors, and if one counts the relaxation time τ_γ as $s + 1$ - fold, one returns directly to (32).

6. The Thermodynamic Potentials in the After-effect Interpretation.

First of all we eliminate the ξ^a in (11) and obtain

$$u - u^+ = T^+ \varepsilon^0 + \frac{1}{2} c_{ik} \varepsilon^i \varepsilon^k - \varepsilon^i \frac{Q_{i\gamma} Q_{k\gamma}}{1 + \tau_\gamma D} \varepsilon^k + \frac{1}{2} \left(\frac{Q_{i\gamma}}{1 + \tau_\gamma D} \varepsilon^i \right) \cdot \left(\frac{Q_{k\gamma}}{1 + \tau_\gamma D} \varepsilon^k \right), \quad (43)$$

whence, by (37) and (32), it follows further that

$$u(t) - u^+ = T^+ \varepsilon^0(t) + \frac{1}{2} c_{ik} \varepsilon^i(t) \varepsilon^k(t) - \varepsilon^i(t) \int_0^\infty c_{ik}(v) \varepsilon^k(t-v) dv - \frac{1}{2} \int_0^\infty \int_0^\infty c'_{ik}(v+w) \varepsilon^i(t-v) \varepsilon^k(t-w) dv dw; \quad (44)$$

where $c'_{ik}(v+w)$ means the derivative with respect to the argument.

Correspondingly we obtain from (17)

$$g(t) - g^+ = -s^+ \sigma_0(t) - \frac{1}{2} c^{ik} \sigma_i(t) \sigma_k(t) + \sigma_i(t) \int_0^\infty c^{ik}(v) \sigma_k(t-v) dv - \frac{1}{2} \int_0^\infty \int_0^\infty c^{ik'}(v+w) \sigma_i(t-v) \sigma_k(t-w) dv dw. \quad (45)$$

Further we have

$$T^+[s(t) - s^+] = u(t) - u^+ - \frac{1}{2} c_{ik} \bar{\varepsilon}^i(t) \bar{\varepsilon}^k(t) + \bar{\varepsilon}^i(t) \int_0^\infty c_{ik}(v) \bar{\varepsilon}^k(t-v) dv + \frac{1}{2} \int_0^\infty \int_0^\infty c'_{ik}(v+w) \bar{\varepsilon}^i(t-v) \bar{\varepsilon}^k(t-w) dv dw, \quad (46)$$

if we put

$$\bar{\varepsilon}^0 = \frac{u - u^+}{T^+}, \quad \bar{\varepsilon}^i = \varepsilon^i (i = 1, 2, \dots, 6). \quad (47)$$

An analogous representation may be obtained for the free energy.

From these results it therefore follows that the thermodynamic potentials at time t may also be represented by the values of their independent variables at time t and at earlier times and also that only the after-effect matrices enter into them. The same statement is true for the local entropy generation

$$A_a \frac{d\xi^a}{dt} = \int_0^\infty \int_0^\infty c_{ik}(v+w) \frac{d\varepsilon^i(t-v)}{dt} \frac{d\varepsilon^k(t-w)}{dt} dv dw = \int_0^\infty \int_0^\infty c^{ik}(v+w) \frac{d\sigma_i(t-v)}{dt} \frac{d\sigma_k(t-w)}{dt} dv dw. \quad (48)$$

7. Theorems on Relaxation Spectra.

If, after some preceding strain and entropy changes, we hold all the ε^i constant with respect to time from $t = 0$ onwards, then from $t = 0$ onwards the ξ^a given by (24) adjust themselves to equilibrium values. Then for $t > 0$ every ξ^a can be written as a sum of exponential functions with exponents $-t/\tau_a$, apart from a constant (the term containing ε^i). We call the τ_a the relaxation times for constant ε^i and their totality we call the relaxation spectrum $\text{Sp}(\varepsilon^0, \dots, \varepsilon^6)$ for constant ε^i ; we count each relaxation time n times, where n = its multiplicity. In the dynamic equation of state (29) not all the τ_γ need occur; for, all $Q_{i\gamma}$ ($i = 0, 1, \dots, 6$) can vanish for certain γ . We want to denote the τ_γ , actually appearing in (29) and different from one another, as the effective relaxation spectrum, i.e. operative for the thermoelastic relations (29), $\text{Sp}_{\text{eff}}(\varepsilon^0, \dots, \varepsilon^6)$ for constant ε^i . If we ask further how a definite one of the σ_i , perhaps σ_q , approaches the equilibrium value for constant ε^i , then under the circumstances again only a subset of the effective relaxation times is of significance; we call them briefly the q -effective relaxation times and their totality the q -effective relaxation spectrum for constant ε^k , and use the notation $\text{Sp}_{\text{eff}}(q; \varepsilon^0, \varepsilon^1, \dots, \varepsilon^6)$ for it.

One can now define relaxation spectra for other conditions, while one holds constant, instead of all ε^i , only some of them and, in addition, the σ_k for the remaining indices. Such a choice we call a 'selection' of variables. As an example, we therefore investigate the spectrum for constant $\varepsilon^0, \varepsilon^1, \dots, \varepsilon^q, \sigma_{q+1}, \dots, \sigma_6$ and call it the spectrum for this selection of variables. Hence we solve equation (13) for $\sigma_0, \sigma_1, \dots, \sigma_q, \varepsilon^{q+1}, \dots, \varepsilon^6$ and obtain

$$\begin{aligned}\sigma_i &= \sum_{k=0}^q l_{ik} \varepsilon^k + \sum_{k=q+1}^6 m_{ik} \sigma_k + \phi_{ia} \xi^a \quad (i = 0, 1, \dots, q), \\ \varepsilon^i &= - \sum_{k=0}^q m_{ki} \varepsilon^k + \sum_{k=q+1}^6 n_{ik} \sigma_k + \psi_{ia} \xi^a \quad (i = q+1, \dots, 6), \\ A_a &= - \sum_{k=0}^q \phi_{ka} \varepsilon^k + \sum_{k=q+1}^6 \psi_{ka} \sigma_k - \rho_{a\beta} \xi^\beta \quad (a = 1, 2, \dots, n). \quad (49)\end{aligned}$$

The summation convention is now valid only with respect to α . The relations $l_{ik} = l_{ki}$, $n_{ik} = n_{ki}$ and $\rho_{\alpha\beta} = \rho_{\beta\alpha}$, as well as the chosen signs follow immediately from the fact that the linear relations (49) can be derived from a potential ψ with the differential

$$d\psi = \sum_{k=0}^q \sigma_k d\varepsilon^k - \sum_{k=q+1}^6 \varepsilon^k d\sigma_k - A_\alpha d\xi^\alpha$$

Further, it follows immediately from the evaluation of $u = u^+ + \frac{1}{2} \sigma_1 \varepsilon^1 - \frac{1}{2} A_\alpha \xi^\alpha$ that l_{ik} , n_{ik} and $\rho_{\alpha\beta}$ belong to positive definite quadratic forms. In addition, we still have the relations

$$E_{\alpha\beta} \frac{d\xi^\beta}{dt} = A_\alpha \quad (\alpha = 1, 2, \dots, n). \quad (50)$$

By a suitable linear transformation of the ξ^α , we now restore $\rho_{\alpha\beta}$ to the form $\delta_{\alpha\beta}$ and $E_{\alpha\beta}$ to the form $\tau_\alpha \delta_{\alpha\beta}$. The τ_α are then obviously the relaxation times for constants $\varepsilon^0, \dots, \varepsilon^q, \sigma_{q+1}, \dots, \sigma_6$. If we assume on the other hand $\varepsilon^0, \dots, \varepsilon^{q-1}, \sigma_q, \dots, \sigma_6$ constant, then by (49) and (50)

$$(1 + \tau_\alpha D) \xi^\alpha = \frac{\phi_{\alpha q} \phi_{q\beta}}{1_{qq}} \xi^\beta$$

-with no loss in generality, we put $\varepsilon^0 = \dots = \varepsilon^{q-1} = \sigma_q = \dots = \sigma_6 = 0$, which is equivalent to replacing the ξ^α by the differences of the ξ_α and their equilibrium values for constants $\varepsilon^0, \dots, \sigma_6$. The solutions of this system of equations are again sums of exponential functions with exponents $-t/\tau_\alpha$ and one shows, just as in ⁹ taking into account $1_{qq} > 0$, that by ordering the τ_α and the $\bar{\tau}_\alpha$ by magnitude

$$\bar{\tau}_1 \leq \bar{\tau}_1 \leq \bar{\tau}_2 \leq \bar{\tau}_2 \leq \dots \leq \bar{\tau}_n \leq \tau_n \quad (51)$$

is true. We write briefly for this

$$Sp(\varepsilon^0, \dots, \varepsilon^{q-1}, \varepsilon^q, \sigma_{q+1}, \dots, \sigma_6) \leq Sp(\varepsilon^0, \dots, \varepsilon^{q-1}, \sigma_q, \sigma_{q+1}, \dots, \sigma_6)$$

and, in particular, write here $<$ instead of \leq if in (51) the equality sign is nowhere valid. In words, we say that the first spectrum is 'not larger' than the second, or in the other case that the first spectrum is 'smaller' than the second. Note that the \leq - or $<$ - relation defined in this way is not transitive; in fact, if $Sp_1 < Sp_2$ and $Sp_2 < Sp_3$ are true, then the

relaxation times of the first spectrum are certainly smaller than those of the third spectrum, however they need not be interlaced. Since the special choice of variables to be held constant is obviously immaterial for this result, we can state the following in general:-

If one replaces a specific extensive variable ε^q by the corresponding intensive variable σ_q , in a selection of variables ε^i, σ_k (the totality of the indices of the ε^i and σ_k therefore contains each of the numbers from 0 to 6 exactly once), then the relaxation spectrum for the system is not diminished.

We now consider further the two spectra

$$Sp_{eff}(q; \varepsilon^0, \varepsilon^1, \dots, \varepsilon^q, \sigma_{q+1}, \dots, \sigma_6)$$

and

$$Sp_{eff}(q; \varepsilon^0, \varepsilon^1, \dots, \varepsilon^{q-1}, \sigma_q, \dots, \sigma_6)$$

By eliminating the ξ^a from (49) and (50) with $\varepsilon^0 = \dots = \varepsilon^{q-1} = \sigma_{q+1} = \dots = \sigma_6 = 0$, we obtain

$$\sigma_q = \left(l_{qq} - \frac{\phi_{qa} \phi_{qa}}{1 + \bar{\tau}_a D} \right) \varepsilon^q. \quad (52)$$

The right side can be written as a rational function in D with n_{eff} as the degree of denominator and numerator, if n_{eff} is the number of the $\bar{\tau}_a$ actually appearing in (52) and different from each other. While the $\bar{\tau}_a$ make up the spectrum

$$Sp_{eff}(q; \varepsilon^0, \varepsilon^1, \dots, \varepsilon^q; \sigma_{q+1}, \dots, \sigma_6)$$

one obtains the spectrum

$$Sp_{eff}(q; \varepsilon^0, \varepsilon^1, \dots, \varepsilon^{q-1}, \sigma_q, \dots, \sigma_6),$$

if one looks for the zeros of the numerator of the rational function mentioned and puts them equal to the negative reciprocal relaxation times of the latter spectrum. From the behavior of the rational function for $D \approx -1/\bar{\tau}_a$ and because $l_{qq} - \phi_{qa}\phi_{qa} \geq 0$, it follows that

$$Sp_{eff}(q; \varepsilon^0, \dots, \varepsilon^q, \sigma_{q+1}, \dots, \sigma_6) < Sp_{eff}(q; \varepsilon^0, \dots, \varepsilon^{q-1}, \sigma_q, \dots, \sigma_6).$$

The effective relaxation times of these two spectra are therefore different from each other in that between every two times of the one spectrum lies

one of the other and the smallest relaxation time of the first spectrum is smaller than that of the other. Also we can generalize this result as follows:-

If one replaces a specific extensive variable ε^q by a corresponding intensive variable σ_q in a selection of variables ε^i, σ_k , then the q-effective relaxation spectrum is enlarged.

If, in particular, $l_{qq} - \rho_{qa}\rho_{qa} = 0$ is true, then a relaxation time of the second spectrum is infinitely large and we have viscoelasticity.

The two theorems obtained are independent of, and thereby valid for, whichever spatial coordinate system the σ_i, ε^i are referred to. However, in the proof we have never employed the fact that the σ_i, ε^i for $i \neq 0$ are components of the stress- and strain-tensors, but only made use of the fact that the linear relations (13) may be derived from a positive definite quadratic form (14) over the differential relations (12). Therefore, the two theorems on relaxation spectra are also valid if, instead of the σ_i, ε^i , we use any linear combinations $\bar{\sigma}_1 = u_{i.}^k \sigma_k$ and, as conjugate quantities, the $\bar{\varepsilon}^k$ determined by $\varepsilon^i = u_{k.}^i \bar{\varepsilon}^k$, where $\det |u_{k.}^i| \neq 0$ has been assumed. This fact is important, for example, if one considers the relaxation between pressure and volume. Then it depends on the connection between $\sigma_1 + \sigma_2 + \sigma_3$ and $\varepsilon^1 + \varepsilon^2 + \varepsilon^3$ perhaps for constant shear deformations or constant shear stresses with, in addition, constant temperature or entropy. It follows on putting

$$\bar{\varepsilon}^1 = \frac{1}{\sqrt{3}} (\varepsilon^1 + \varepsilon^2 + \varepsilon^3), \bar{\varepsilon}^2 = \frac{1}{\sqrt{6}} (\varepsilon^1 + \varepsilon^2 - 2\varepsilon^3), \bar{\varepsilon}^3 = \frac{1}{\sqrt{2}} (\varepsilon^1 - \varepsilon^2)$$

and

$$\bar{\sigma}_1 = \frac{1}{\sqrt{3}} (\sigma_1 + \sigma_2 + \sigma_3), \bar{\sigma}_2 = \frac{1}{\sqrt{6}} (\sigma_1 + \sigma_2 - 2\sigma_3), \bar{\sigma}_3 = \frac{1}{\sqrt{2}} (\sigma_1 - \sigma_2)$$

and retaining the other σ_i, ε^i with the indices $i = 0, 4, 5, 6$. Then, as 'selections' of variables $\varepsilon^0, \bar{\varepsilon}^1, \bar{\varepsilon}^2, \dots, \varepsilon^6$ and $\varepsilon^0, \bar{\sigma}_1, \bar{\varepsilon}^2, \dots, \bar{\varepsilon}^6$ are to be chosen for adiabatic conditions. For isothermal conditions, in both selections ε^0 is to be replaced by σ_0 .

These statements on the relaxation spectra are valid in the same way for discrete relaxation spectra with infinitely many relaxation times, and are also valid for continuous relaxation spectra. From the relation (51)

it follows in particular that, if the spectrum of the $\bar{\tau}_a$ fills a finite continuous interval $a \leq \bar{\tau}_a \leq b$, the spectrum of the $\bar{\tau}_a$ fills the same continuous interval; there is however, at least in those cases where one deals with a q-effective spectrum, as one sees in particular examples (see ¹⁰), still an isolated relaxation time $\bar{\tau}_1 < a$ outside this interval. A corresponding statement is true, if the $\bar{\tau}_a$ fills a continuous interval $a \leq \bar{\tau}_a \leq b$; then there is an isolated relaxation time $\bar{\tau} > b$.

The statements of this section are closely connected with the principle of Le Chatelier-Braun.

8. Periodic Changes of State

If the ε^i are periodic functions of the time with time dependence $e^{i\omega t}$, then it follows from (29) that

$$\sigma_i = \left[c_{ik} - \frac{Q_{i\gamma} Q_{k\gamma}}{1 + i\omega\tau_\gamma} \right] \varepsilon^k, \quad (53)$$

i.e. the connection between the σ_i and ε^i is formally the same as in the equilibrium ($\omega = 0$), but with a frequency dependent complex thermoelastic matrix.

For slow changes of state, for which

$$\omega\tau_s \ll 1 \text{ for } s = m+1, m+2, \dots,$$

one can write as an approximation

$$\sigma_i = \left\{ \left[c_{ik} - \sum_{\gamma=m+1}^n Q_{i\gamma} Q_{k\gamma} \right] - \sum_{\gamma=1}^m \frac{Q_{i\gamma} Q_{k\gamma}}{1 + i\omega\tau_\gamma} + i\omega \sum_{\gamma=m+1}^{\infty} Q_{i\gamma} Q_{k\gamma} \tau_\gamma \right\} \varepsilon^k.$$

Among these assumptions the fastest relaxation phenomena have been regarded as having practically died out: they make themselves felt only in a formal change of the thermoelastic matrix $c_{ik} \rightarrow c_{ik} - \sum_{\gamma=m+1}^n Q_{i\gamma} Q_{k\gamma}$ - it corresponds

to a thermodynamic equilibrium for which the fast relaxation processes have died away and the slow are continuing - and in an extra term of viscous character proportional to it. Here it is not a question of a proper viscosity, as one sees if one solves (53) for the ε^k and then again approximates for the fast relaxation processes in the same way as above; in fact there is no term

of the sum with the factor $(i\omega)^{-1}$. On the contrary, proper viscous behavior (viscoelasticity) exists, as we have already noted, only if

$$\det \left| c_{ik} - Q_{i\gamma} Q_{k\gamma} \right| = 0.$$

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